HOT GAS DESULFURIZATION WITH Z-SORB® SORBENTS

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Introduction

Originally designed as a sorbent for tail gas cleanup [1], Phillips Z-Sorb® Sorbent has found application for the removal of hydrogen sulfide from the fuel gas that is generated in a clean coal process. For the latter technology, previous fixed bed sorbents have shown poor mechanical stability due to spalling when adsorbing hydrogen sulfide in reducing gas atmospheres or when being regenerated over many cycles [2].

Bench scale fixed-bed tests conducted at the Morgantown Energy Technology Center showed that Z-Sorb® sorbent performed better than zinc titanate [3,4]. The performance of the sorbent in a moving-bed application at General Electric was very encouraging [5]. The sorbent flowed well, H2S was reduced to less than 50 ppm at the absorber outlet over long periods and post-test analyses of the sorbent indicated very low sulfate levels at the regenerator exit. The fluidizable version of the novel sorbent was initially tested in Research Triangle Institute's high temperature, high pressure, semi-batch, fluidized-bed reactor system [6]. In a life cycle test consisting of 50 cycles of sulfidation and regeneration, this sorbent exhibited excellent activity and regenerability. The sulfur loading was observed to be 90+ percent of the theoretical capacity. The sorbent consistently demonstrated a sharp regeneration profile with no evidence of sulfate accumulation.

Tests with Z-Sorb® sorbents for desulfurization of coal derived gases were conducted at moderate pressure (507-2027 kPa) and a broad range of operating temperatures (315-540 °C). Earlier studies emphasized the upper end of this temperature range since it is proposed for most gasification projects [4, 7, 8]; other studies have shown the new sorbent formulations operate at lower temperatures (315-425 °C) [1, 4, 9]. These sorbents fulfill the requirements of long term sorbent reactivity, chemical/mechanical stability and attrition resistance.

This paper will provide a summary of the performance of Phillips proprietary Z-Sorb® sorbents at a number of test locations in the United States and Europe. Project participants working with Phillips in this study have been the M. W. Kellogg Company, General Electric (GE), Research Triangle Institute (RTI), Morgantown Energy Technology Center (METC) and members of the European Coal and Steel Community (ECSC).

Sorbent Characteristics

A sorbent for hot gas desulfurization must demonstrate high chemical reactivity, as measured by the rate of sulfur absorption and the sulfur loading capacity, and physical integrity. In addition, for fluidized-bed/transport reactor operation the sorbent must also have good fluidizing characteristics and mechanical strength characterized by low attrition losses. Phillips Petroleum Company has developed suitable sorbent for each of the reactor types currently being developed for the hot gas desulfurization technology. Extruded, spherical, and granular Phillips sorbent formulations are now available for fixed-bed, moving-bed, and fluidized-bed/transport reactor systems, respectively. For fixed-bed reactor the sorbent used was in an extruded form consisting of 1/8" pellets having a bulk density of about 1.0 g/cc. A fluidized version of Phillips' sorbent had an average particle size of 175 micron, a particle size range of 50-300 micron and an apparent bulk density of 0.90-1.00 g/cc. For a moving-bed reactor, a spherical sorbent with an average pellet diameter of 4.1 mm and bulk density of 0.96 g/cc was used.

Bench/Pilot Scale Testing

Phillips Petroleum Company has conducted extensive testing of its proprietary Z-Sorb® sorbent with several research partners in the United States and Europe. Table I summarizes the important parameters from each of these tests. The data reveals a number of facts. It is evident that this sorbent has a high chemical reactivity for sulfur capture. Generally, a sulfur loading of 15-20 wt% is easily achieved. The most striking feature of this sorbent was its high efficiency for sulfur removal with a very sharp breakthrough. Removal of sulfur in various fuel gases to less than 10 ppm under most conditions and perhaps close to zero ppm under some conditions has been demonstrated [4, 10-15]. The data presented in Table I also show that sulfur removal ability of this sorbent is totally unaffected by the gas

composition. The sorbent appears to be effective in removing sulfur from a broad composition range of fuel gases produced by different types of gasifiers ranging from KRW to Shell.

The application of Z-Sorb® sorbent in removing sulfur from authentic gasifier product gases generated from biofuel/brown-coal was investigated by TPS Termiska Processor AB (Sweden). Of the various commercially available sorbent tested, this study found Z-Sorb® sorbent to be the most promising. The sorbent reduced the sulfur content in the effluent stream to below 10 ppm and fully reactivated after desorption at steam concentrations up to 15% at pressures up to 20 bar. Z-Sorb® sorbent was also less sensitive to steam concentration than a zinc titanate sorbent, ZT-4 [11].

Recent work with modified formulations suggests the sorbent temperature application range can be expanded to include the lower temperatures (260-430 °C) used for moderate temperature gas cleanup. Our research found that zinc oxide-based sorbents are effective in desulfurization above 315 °C. Even at temperatures of 315-430 °C the sulfur capacity retained forty to fifty percent of a typical value obtained at higher temperatures, such as 540 °C. Figure 1 gives the bench scale test results for the temperature dependence of the sulfur loading capacity of Z-Sorb® sorbent. These runs were done at atmospheric pressure with 4.2% H_2S in CO_2/N_2 and a gas hourly space velocity of 1440 h^{-1}. The sorbent was a fluid bed material. Sulfur loadings of 6-22 wt% in the temperature range of 315-650 °C are quite suitable for a variety of processes currently under development in the Integrated Gasification Combined Cycle (IGCC) program. We also have Thermogravimetic Analysis (TGA) reactivity data that amplify these results. Figure 2 presents the chemical reactivity of a fresh sorbent exposed to simulated coal gases at different temperatures. There is a slight fall-off in sulfur loading as the temperature of absorption is reduced from 540 °C to 370 °C, but the rate at which hydrogen sulfide is absorbed does not suffer as much.

In the long-term bench testing at Phillips Petroleum, the sulfur loading capacity of Z-Sorb® sorbent was found to remain high over a large number of cycles. Figure 3 shows the remarkable performance of an extruded, fixed-bed formulation at an absorption temperature of 430 °C. For nearly 700 cycles of absorption and regeneration, the loadings remain at a high level, starting at 14% and ending at 8%. For most of the cycles, the sorbent picked up at least 10% sulfur, which is 50% of the theoretical loading.

Problem of Sulfate Formation

One of the major concerns in developing regenerable sorbent is formation and accumulation of sulfates in the sorbent during multi-cycle use. Accumulation of sulfates is not desirable as it not only affects the sulfur removal efficiency of the sorbent, but in some cases, for example in zinc titanate sorbents, it has been shown to cause spalling of pellets resulting in fatal failures during process. Although, this problem is not prevalent in Z-Sorb® sorbents as the total sulfur content in the regenerated samples is normally less than 0.5 weight percent, we investigated the regeneration step in detail to examine conditions for the formation of sulfates. Thermogravimetric analysis was used to investigate the regeneration kinetics of a single pellet of sulfided Z-Sorb® sorbent and corresponding x-ray photoelectron spectroscopy (XPS) analysis of the regenerated pellet was performed. A sulfided sample was used for this analysis. It had about ten weight percent sulfur on it. As drawn in Figure 4, the weight loss curves for a single pellet regenerated at different temperatures from 480 °C to 755 °C indicate that 480 °C and 540 °C are ineffective in completely regenerating the sulfided absorbent. In fact, the sample at 480 °C gained weight. XPS measurements in Figure 5 agree on this point. The binding energy data of sulfur from XPS reveal a large amount of sulfide sulfur and sulfate sulfur on the sample after regeneration at 480 °C. Apparently, zinc sulfide converted to zinc sulfate, thereby increasing the weight of the sample. The 540 °C sample showed lower sulfide and sulfate sulfur, but there still was sufficient sulfide to show that regeneration was incomplete. By 565 °C, there was no sulfide left, and by 755 °C, there was no sulfate left. This finding is in agreement with the decomposition temperature of zinc sulfate, which is 740 °C [15].

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Table 1. Z-Sorb® Sorbent Testing Summary for Hot Gas Cleanup

Research Partner	Process Type	Test Scale	Operating Temperature (C)	Operating Pressure (kPa)	Regeneration Temperature (C)	Coal Gas	Sulfur Loading (gS/100g Sorbent)	Effluent Sulfur (ppmv)	Ref.
DOE Morgantown	Fixed Bed	Laboratory	538	1038	482-732	Simulated KRW	14	0	4
CTDD of British Coal	Fixed Bed	Pilot Plant	540	1051	540-760	Air-Blown Gasifier	10.5	<10	10
CIEMAT	Fixed Bed	Pilot Plant	400	1050-2027	650	Simulated EcoGas	16.4-16.9	<20	
TPS	Fixed Bed	Laboratory	480	1050-2027	650	BioMass/Brown Coal	not det.	4.7	11
General Electric	Moving Bed	Laboratory, Pilot Plant	538	2027	730	Lurgi Gasifier		<50	12
Research Triangle Institute	Fluid Bed	Laboratory	538	2027	580-780	Simulated U-Gas	10.0-20.2	10	13
CTDD of British Coal	Fluid Bed	Pilot Plant	520-540	1051	575-717	Airblown Gasifier	13-15	<10	10
Research Laboratory A	Fluid Bed	Laboratory	400	2027	600	Shell Type	17.5-20.3	<1	14
M W KeCogg	Fluid Bed	Pilot Plant	538-565	690	538	1% H2S in N2	15.4	0	15

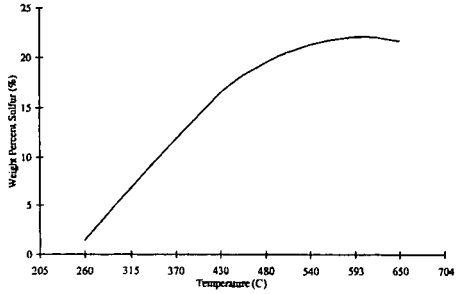

Figure 1. Sulfur Loading Capacity as a Function of Temperature

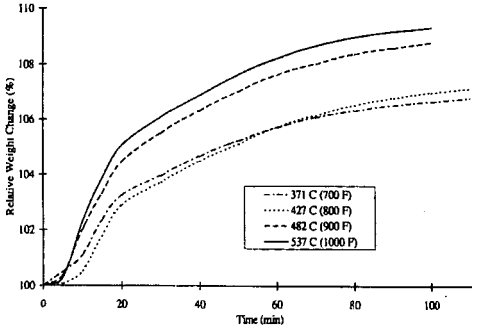

Figure 2. TGA Sulfur Loading Capacity

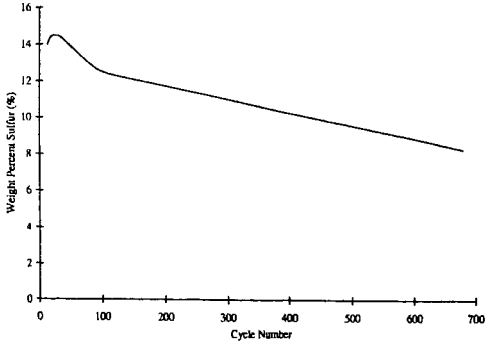

Figure 3. Sulfur Loading Capacity as a Function of Cycle

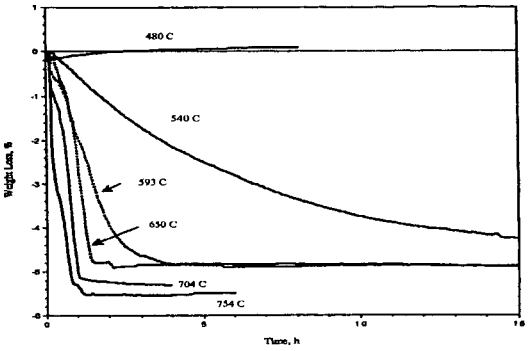

Figure 4. TGA Analysis for Sulfided Z-Sorb® Sorbent

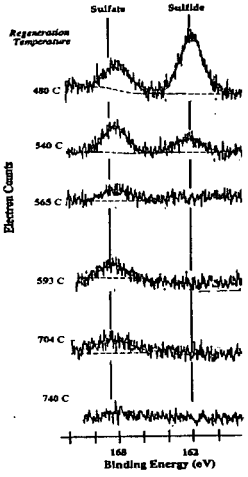

Figure 5. Z-Sorb® Sorbent XPS Analysis of Regenerated Samples